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Chemiluminescence in the Gas Phase Reaction"

**XXV Informal Conference on Photochemistry**  
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(Statement A)

# Kinetics of CH Radicals With O<sub>2</sub>: Evidence for CO-Chemiluminescence in the Gas Phase Reaction

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The methylidyne (CH) radical is known to be an important reaction intermediate during the oxidation of hydrocarbon fuels. Its reactivity with combustion species such as O<sub>2</sub>, O-atoms, CO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, NH<sub>3</sub> and numerous other hydrogenous, carbonaceous and sulfurous species is well reviewed<sup>1,2</sup> and compiled in the literature.<sup>3</sup> However, the nature of product branching, energy disposal and its theoretical treatment has been examined in only a few of these reactions; (CH + NO) and (CH + N<sub>2</sub>) reactions by far being the most studied systems. Particularly lacking in the literature is information on the production of electronically excited state species. The Air Force Research Laboratory is interested in the methylidyne and the methylene (CH<sub>2</sub>) radical reactions with O<sub>2</sub> and O-atoms since they are thought to play an important role in the production of ultraviolet/visible chemiluminescence when rocket plumes interact with the earth's ambient atmosphere.<sup>4</sup>

Production of CO vis-uv-chemiluminescence has been observed for the first time in the gas phase reaction of the methylidyne radicals with molecular oxygen. A trace amount of CHBr<sub>3</sub> vapor was photo-decomposed in a pulsed-photolysis reactor using a 248-nm laser under multi-photon-dissociation conditions to produce the CH(X<sup>2</sup>Π) radicals in an excess of O<sub>2</sub> in diluent helium carrier gas at 2.0 torr and 298 K. The time resolved chemiluminescent traces due to characteristic CO(A-X), CO(a-X) and CO(d-a) vibronic emissions were recorded at several band positions. 147.8 nm was the shortest wavelength at which CO emission was recordable. The integrated intensities of the CO emissions showed a quadratic dependence on the photolysis fluence employed as did the OH(A-X) emission in the (1-0) band. The dependence of the OH and CO chemiluminescence on [O<sub>2</sub>] was studied to obtain the rate coefficient(s) for the chemiluminescent reaction(s). The data is best interpreted by postulating that CH(v"≥0) reactions with O<sub>2</sub> lead to the observed CO-emissions as well as the well-known<sup>5-7</sup> OH-chemiluminescence.

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